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I, Japanese Patent Attorney Yoshitaka OSHIDA, having my office at GINZA BUILDING 3-12, 3-CHOME, GINZA CHUO-KU, TOKYO, JAPAN, do solemnly and sincerely declare:

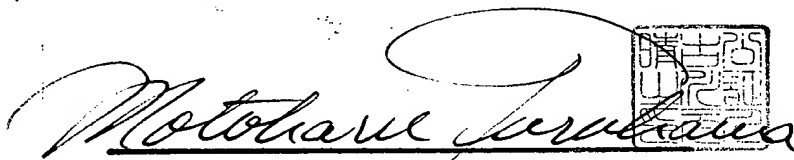
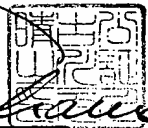
1. That I am well acquainted with the Japanese and English languages, and
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And I make this solemn declaration conscientiously believing the same to be true and correct.


Yoshitaka OSHIDA

Affirmed before me

May 13, 2004

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証

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平成16年 5 月 13 日、本公証人役場において

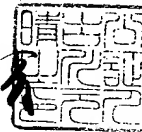
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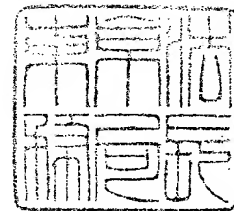
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平成16年 5 月 13 日

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APOSTILLE

(Convention de La Haye du 5 octobre 1961)

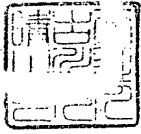
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JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this office.

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Applicant(s): NEOMAX CO.,LTD.

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Commissioner, Japan Patent Office: Yasuo IMAI

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Specification

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Abstract

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yes

【Name of Document】 Specification

【Title of Invention】 THERMOELECTRIC CONVERSION MATERIAL,
AND METHOD FOR MANUFACTURING THE SAME

【What is claimed is】

【Claim 1】 A thermoelectric conversion material having a structure in which added elements to make a p-type or n-type semiconductor are contained in an amount of 0.001 to 20 at% in silicon, either singly or in combination, and said added element-rich phase is formed in the grain boundary of a silicon-rich phase composed chiefly of silicon.

【Claim 2】 The thermoelectric conversion material according to claim 1, wherein at least each one type of added elements (added elements α) to make a p-type semiconductor and added elements (added elements β) to make an n-type semiconductor is contained in an amount of 0.002 to 20 at% in total amount, and the total amount of the added elements α or β is contained by the amount required to make a p-type or n-type semiconductor over the total amount of the relative added elements α or β .

【Claim 3】 The thermoelectric conversion material according to claim 1 or 2, wherein added elements to make a p-type semiconductor (added elements α) are one or more types selected from each group consisting of added elements A (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl) and transition metal elements M₁ (Y, Mo, Zr), and added elements

to make an n-type semiconductor (added elements β) are one or more types selected from each group consisting of added elements B (N, P, As, Sb, Bi, O, S, Se, Te), transition metal elements M_2 (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au; where Fe accounts for 10 at% or less), and rare earth elements RE (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu).

【Claim 4】 The thermoelectric conversion material according to claim 1, wherein Group III-V compound semiconductors or Group II-VI compound semiconductors are contained in an amount of 1 to 10 at%, and further at least one type of the added elements A (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl) or the added elements B (N, P, As, Sb, Bi, O, S, Se, Te) is contained in an amount of 1 to 10 at%.

【Claim 5】 The thermoelectric conversion material according to claim 1, wherein at least one type of Ge, C and Sn is contained in an amount of 0.1 to 5 at%, one or more types selected from each added element group consisting of the added elements A (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl) or the added elements B (N, P, As, Sb, Bi, O, S, Se, Te) are contained.

【Claim 6】 A method for manufacturing the thermoelectric conversion material, wherein a structure where said added element-rich phase is formed in the grain boundary of a silicon-rich phase composed mainly of silicon

can be obtained by melting the added elements to make a p-type or n-type semiconductor such that added elements are contained in an amount of 0.001 to 20 at%, either singly or in combination, in silicon and quenching a melt.

【Claim 7】 The method for manufacturing the thermoelectric conversion material according to claim 6, wherein the melting method is arc melting or high-frequency melting.

【Claim 8】 The method for manufacturing the thermoelectric conversion material according to claim 6, wherein the melting and cooling methods are any of CZ method, FZ method or ZL method.

【Detailed Description of the Invention】

【0001】

【Technical Field of the Invention】

This invention relates to a novel thermoelectric conversion material in which silicon is made to contain various types of added element at an amount of 20 at% or less, and more particularly relates to a polycrystal silicon-based thermoelectric conversion material, characterized in that by making an added element-rich phase dispersed in the grain boundary of a silicon-rich phase, Seebeck coefficient becomes extremely large and thermal conductivity low, allowing the thermoelectric conversion efficiency to be raised dramatically, and silicon, which is an abundant resource, is chiefly contained and

environmental pollution is extremely little.

【0002】

【Background Art】

Thermoelectric conversion elements are devices that are expected to see practical use because of their efficient utilization of the high levels of thermal energy required in recent industrial fields. An extremely broad range of applications have been investigated, such as a system for converting waste heat into electrical energy, small, portable electric generators for easily obtaining electricity outdoors, flame sensors for gas equipment, and so forth.

【0003】

This conversion efficiency from thermal energy to electrical energy is a function of the Figure of merit ZT , and rises in proportion to ZT . This Figure of merit ZT is expressed by Formula 1.

$$ZT = \alpha^2 \sigma T / \kappa$$

Formula 1

Here, α is the Seebeck coefficient of the thermoelectric material, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature expressed as the average value for the thermoelectric element on the high temperature side (T_H) and the low temperature side (T_L).

【0004】

Silicides such as FeSi_2 and SiGe , which are

thermoelectric conversion materials that have been known up to now, are abundant natural resources, but the former has a Figure of merit ZT of 0.2 or less, its conversion efficiency is low, and its usable temperature range is extremely narrow, while no decrease in thermal conductivity is seen with the latter unless the germanium content is about 20 to 30 at%, and germanium is a scarce resource. Also, silicon and germanium have a state in which there is a broad liquidus and solidus for complete solid solution, and it is difficult to produce a uniform composition with melting or ZL (zone leveling), to impede industrial application. For these reasons, the above-mentioned materials have not found widespread use.

【0005】

The thermoelectric materials with the highest Figure of merit at the present time are IrSb_3 , having a skutterudite-type crystal structure, and BiTe , PbTe , and other such chalcogen compounds, which are known to provide highly efficient thermoelectric conversion capability, but from the standpoint of protecting the global environment, the use of these heavy metal elements is expected to be restricted in the future.

【0006】

【Problems to be solved by the Invention】

Silicon, meanwhile, has a high Seebeck coefficient, but has extremely high thermal conductivity, and is

therefore not considered suitable as a high efficiency thermoelectric material, and research into the thermoelectric characteristics thereof has been limited to silicon with a carrier concentration of $10^{18}(\text{Mm}^3)$ or less.

【0007】

The inventors discovered that doping silicon single piece with various elements, such as doping silicon with both a trace amount of a Group III element or Group V element and a small amount of germanium, makes it possible to lower thermal conductivity, and the Seebeck coefficient will be equivalent to or better than that of conventional Si-Ge and Fe-Si compounds, or will be extremely high at a given carrier concentration. They also discovered that this material exhibits a good Figure of merit as a thermoelectric conversion material, without losing the fundamental advantages afforded by silicon single piece.

【0008】

The inventors also produced p- and n-type semiconductors by doping a silicon with various elements, and examined the relationship of the doping amount to the thermoelectric characteristics, and as a result found that up to an added amount (that is, a carrier concentration) of $10^{18}(\text{M/m}^3)$, the Seebeck coefficient decreases in inverse proportion to the carrier concentration, but has a maximum value from 10^{18} to $10^{19}(\text{M/m}^3)$.

【0009】

It is an object of the present invention to further lower thermal conductivity or further enhance the Seebeck coefficient and thereby improve performance, without sacrificing the high Seebeck coefficient and electrical conductivity had by this novel silicon-based thermoelectric conversion material discovered by the inventors.

【0010】

【Means to solve the Problems】

The inventors diligently examined the mechanism by which a high Seebeck coefficient is obtained with a silicon-based thermoelectric conversion material doped with various added elements, whereupon they learned that this novel silicon-based material has a structure in which at the grain boundary of a silicon-rich phase containing mainly silicon, an added element-rich phase is formed.

【0011】

The inventors also investigated a crystal structure, and they discovered that since the added element cohesion occurs at the crystal grain boundary and the conduction of carriers can be increased, a high Seebeck coefficient is obtained in the silicon-rich phase within the crystal grain.

【0012】

In view of this, the inventors tried controlling the crystal structure aside from composition as a method for keeping the Seebeck coefficient high and lowering the thermal conductivity, whereupon they found that if the

cooling rate is controlled during melting and solidification, the silicon-rich phase and added element-rich phase will be dispersed in the required arrangement within the material, and a material having a high Figure of merit will be obtained.

【0013】

That is, the present invention is characterized in obtaining a thermoelectric conversion material having a structure wherein by melting such that one or more added elements (referred as added elements α) to make a p-type semiconductor and added elements (referred as added elements β) to make an n-type semiconductor are contained in silicon in an amount of 0.001 to 20 at%, and quenching the melts, the above-mentioned added element-rich phase is formed at the grain boundary of silicon-rich phase composed mainly of silicon.

【0014】

【Mode of Working of the Invention】

The structure in which the above-mentioned added element-rich phase is formed at the boundary of the silicon-rich phase composed of mainly silicon, which is a characteristic feature of the thermoelectric conversion material of the present invention, will now be described. First, $\text{Si}_{1-x}\text{Ge}_x$ melts (at%) were produced by arc melting, with various added amounts of germanium (4N) into high purity silicon (10N), were quenched at a cooling rate of 50

to 200K/sec after melting to produce sample substrates. The crystal structure was observed by EPMA. As shown in Figure 1A, when $x = 0.03$, the black parts in the photographs are the silicon-rich phase, which is virtually all silicon, although a trace amount of added element is included, and the white parts are the added element germanium rich-phase, and it can be seen that in this structure the germanium-rich phase is formed or dispersed at the grain boundary of the silicon-rich phase.

【0015】

Also, a trace amount of phosphorus was added to the above-mentioned Si-Ge melts, but when just the phosphorus was observed, the EPMA photographs were as shown in Figure 1B, with the white parts indicating places where the doped phosphorus is present, and it can be seen that in this structure the phosphorus is segregated in the same locations where the germanium-rich phase in Figure 1A as mentioned above was formed at the grain boundary of the silicon-rich phase.

【0016】

In other words, the structure of the thermoelectric conversion material of the present invention, as shown by the schematic diagram in Figure 2, is a structure in which are formed a silicon-rich phase consisting of silicon alone or almost entirely of silicon but including a trace amount of added element, and an added element-rich phase in which

an added element is segregated at the grain boundary of this silicon-rich phase. The size of the silicon-rich phase varies with the cooling rate, but is about 10 to 200 μ m.

【0017】

The relationship between carrier concentration of an n-type and p-type silicon and the state of crystal grain boundary deposition of an added element of phosphorus or boron instead of germanium was examined, which confirmed that the relationship of the carrier concentration and the doping amount increased agreeably. Because of the structure in which the added element-rich phase was formed at the grain boundary of the silicon-rich phase, the added element was clumped at the crystal grain boundary, the electrical conductivity resulting from carriers was high, a high Seebeck coefficient was obtained in the silicon-rich phase within the crystal grains.

【0018】

Furthermore, it was confirmed that the thermal conductivity of this silicon-based thermoelectric conversion material decreases as the carrier concentration is increased. This is believed to be because κ_{ph} was decreased by local phonon scattering of impurities resulting from the added element in the crystals.

【0019】

It is believed that a structure in which an added

element-rich phase of germanium or the like is dispersively formed at the grain boundary of a silicon-rich phase, which is a characteristic of a silicon-based thermoelectric conversion material, is obtained by controlling the cooling rate after casting, and that the crystal grain size is kept relatively small by quenching, segregation of a suitable added element other than silicon occurs at the crystal grain boundary, and this results in a high Seebeck coefficient despite the high electrical conductivity.

【0020】

With the silicon-based thermoelectric conversion material of the present invention, the above-mentioned structure is obtained by cooling a silicon-based molten material, and arc melting and high-frequency melting are ideal melting methods for mass production. The cooling rate of the silicon-based molten material is suitably determined by the type and combination of added elements (discussed below), the doping amount, and so forth, as well as the cooling method employed, and the form such as an ingot, a thin sheet, a substrate, or a ribbon.

【0021】

Cooling methods that can be employed in the present invention include cooling the ingot just as it is, and cooling while pulling, such as a method in which a known CZ or FZ method for obtaining monocrystalline silicon is utilized and pulling and cooling are performed under

conditions that allow polycrystalline silicon to be obtained. Because a CZ or FZ method allows numerous substrates of the required thickness to be manufactured from a pulled ingot rod, they are ideal methods for manufacturing a silicon-based substrate for use in thermoelectric conversion elements. Manufacture by ZL method is also possible.

【0022】

Other methods may also be employed, such as a method in which a thin sheet is fabricated by casting and cooling a silicon-based molten material in a shallow plate, or utilizing a roll cooling method such as a known melt quenching method to control the cooling rate so that a thin sheet of the required thickness will be obtained.

【0023】

For instance, when a silicon-based molten material is cast and cooled in a shallow plate, or the plate is water-cooled or brought into contact with a chiller, then cooling at a rate of at least 50K/sec is appropriate, for example, which will keep the crystal grain size to just a few hundred microns or less and result in a high Seebeck coefficient. A preferable cooling rate is 50K/sec to 500K/sec, and it is possible to achieve an average crystal grain size of 30 to 200 μ m.

【0024】

A thermoelectric conversion material according to the present invention is a highly efficient silicon-based

thermoelectric conversion material of a p-type and n-type semiconductor which lowers the electric resistance, improves the Seebeck coefficient and improves dramatically Figure of merit without losing the fundamental advantages afforded by silicon single piece by adding various impurities into the polycrystalline silicon semiconductor having a diamond-like crystal structure and adjusting the carrier concentration.

【0025】

When the applications of a thermoelectric conversion material are considered, emphasis must be placed on one of the characteristics, such as the Seebeck coefficient, electrical conductivity, or thermal conductivity depending on the conditions which vary with the application, such as the heat source, where and how the material is used, and the size of the current and voltage to be handled, but the thermoelectric conversion material of the present invention allows the carrier concentration to be determined by means of the added amount of the selected added element.

【0026】

For example, when one or more elements from the above-mentioned added elements α are contained in an amount of 0.001 to 0.5 at%, a p-type semiconductor with a carrier concentration of 10^{17} to 10^{20} (M/m³) will be obtained, and when added elements α are contained in an amount of 0.5 to 5.0 at%, a p-type semiconductor with a

carrier concentration of 10^{19} to 10^{21} (M/m^3) will be obtained.

【0027】

Similarly, when one or more elements from the above-mentioned added elements β are contained in an amount of 0.001 to 0.5 at%, an n-type semiconductor with a carrier concentration of 10^{17} to 10^{20} (M/m^3) will be obtained, and when added elements β are contained in an amount of 0.5 to 10 at%, an n-type semiconductor with a carrier concentration of 10^{19} to 10^{21} (M/m^3) will be obtained.

【0028】

When the above-mentioned added elements α or added elements β are contained in an amount of 0.5 to 5.0 at% so that the carrier concentration is 10^{19} to 10^{21} (M/m^3), a highly efficient thermoelectric conversion element is obtained, and the thermoelectric conversion efficiency is excellent, but the thermal conductivity thereof is about 50 to 150 W/m · K at room temperature, and if the thermal conductivity could be decreased, there would be a further improvement in the Figure of merit ZT.

【0029】

Generally, the thermal conductivity of solids is given as a sum of the conduction due to phonon and the conduction due to carrier. In case of thermoelectric conversion material of a silicon-based semiconductor, since the carrier concentration is small, the conduction due to

phonon is dominant. Therefore, to decrease the thermal conductivity, it is necessary to make the absorption or scattering of phonon large. In order to make the absorption or scattering of phonon large, it is effective to disturb the regularity of the crystal structure, and the crystal grain size.

【0030】

Then, as the results of various studies about added elements to silicon, it is possible to disturb the crystal structure without changing the carrier concentration in silicon by adding at least one Group III element and at least one Group V element to silicon and controlling the carrier concentration to a range of 10^{19} to 10^{21} (M/m³). It is found that the thermal conductivity can decrease 30 to 90%, to 150 W/m · K or less at room temperature, and a high efficiency thermoelectric conversion material can be obtained.

【0031】

Further, in the above constructed thermoelectric conversion material, a p-type semiconductor will be obtained if the Group III element is contained in an amount 0.3 to 5 at% larger than the Group V element, and an n-type semiconductor will be obtained if the Group V element is contained in an amount 0.3 to 5 at% larger than the Group III element.

【0032】

The inventors also investigated whether a decrease in thermal conductivity could be achieved with something other than Group III elements and Group V elements, and found that the crystal structure can be disturbed without changing the carrier concentration in the silicon, the thermal conductivity can be brought below 150 W/m · K or less at room temperature, and a highly efficient thermoelectric conversion material can be obtained by adding a Group III - V compound semiconductor or a Group II - VI compound semiconductor to silicon, further adding at least one type of Group III element or Group V element and controlling the carrier concentration to a range of 10^{19} to 10^{21} (M/m³).

【0033】

Furthermore, as a result of variously investigating other added elements to silicon, the inventors found that if the silicon contains the Group IV elements germanium, carbon, and tin in an amount of 0.1 to 5 at%, and some of the silicon atoms are replaced with a Group IV element with a different atomic weight, there will be greater phonon scattering in the crystals and the thermal conductivity of the semiconductor can be reduced 20 to 90%, to 150W/m · K or less at room temperature. Further, it is possible to obtain a thermoelectric conversion material wherein a p-type semiconductor is obtained if the Group III element is contained in an amount of 0.1 to 5.0 at% and

furthermore a thermoelectric conversion material wherein an n-type semiconductor is obtained if the Group V element is contained in an amount of 0.1 to 10 at%.

【0034】

Other elements besides the above-mentioned Group III and V elements were examined to see if they could similarly be added to silicon in the thermoelectric conversion material of the present invention, whereupon it was confirmed that while there are no particular restrictions as long as a p- or n-type semiconductor will result, if elements whose ion radii are too different are used, almost all will precipitate in the grain boundary phase, so it is preferable to use an element whose ion radius is relatively close to that of silicon. It is confirmed that one or more elements of the following groups are particularly effective as added elements α to make a p-type semiconductor or as added elements β to make an n-type semiconductor.

【0035】

The added element α are each group consisting of added elements A (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl) and transition metal elements M_1 (Y, Mo, Zr). The added elements β are each group consisting of added elements B (N, P, As, Sb, Bi, O, S, Se, Te), transition metal elements M_2 (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au; where Fe accounts for 10

at% or less), and rare earth elements RE (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu).

【0036】

Further, if, in added elements α to make a p-type semiconductor and added elements β to make an n-type semiconductor, at least one type from each group is contained at an amount of 0.002 to 20 at% in total amounts, for example, if in order to obtain a p-type semiconductor the total amount of added elements α is contained only at the required amount to make a p-type semiconductor over that of added elements β , voluntary combinations of each group can be selected.

【0037】

【Examples】

Example 1

High-purity silicon (10N) and an added element were compounded as shown in Table 1 and then arc-melted in an argon gas atmosphere to produce p- and n-type silicon thermoelectric conversion semiconductors. The temperature in the arc melting was approximately 1900K, and the molten material was cooled at a rate of 50 to 100K/sec by a water-cooled copper base. The average crystal grain size of the obtained material was approximately 50 to 100 μ m.

【0038】

The button-shaped ingots thus obtained were cut to sizes of 5 × 5 × 15 mm, 10 × 10 × 2 mm, and 10

(outside diameter) $\times 2$ mm, and the Seebeck coefficient, Hall coefficient (including carrier concentration and electrical conductivity), and thermal conductivity were measured for each. The measurement values at 1100K and the Figure of merit ($ZT = S^2T/\rho \kappa$) are shown in Table 2.

【0039】

The temperature differential between the high and low temperature portions during temperature elevation was set to be about 6K, the thermoelectromotive force of the samples was measured with a digital multimeter, and this value was divided by the temperature differential to find the Seebeck coefficient. The Hall coefficient was measured by AC method, and the electrical resistance was measured by four-terminal method simultaneously with the carrier concentration. The thermal conductivity was measured by laser flash method.

【0040】

Example 2

In order to produce p- and n-type silicon thermoelectric semiconductors, high-purity silicon (10N) and added elements were compounded as shown in Table 3, after which this product was put in a graphite crucible and melted in a high-frequency melting furnace in a vacuum (10^{-4} Torr). The melting temperature was approximately 1900K, the casting temperature was approximately 1800K, and the melt was cast into a mold with a thickness of 10 mm. The

cooling rate of the molten material was 10 to 50K/sec, and the average crystal grain size of the material was approximately 100 to 500 μ m.

【0041】

The ingots thus obtained were cut to sizes of 5 × 5 × 15 mm, 10 × 10 × 2 mm, and 10 (outside diameter) × 2 mm, and the Seebeck coefficient, Hall coefficient (including carrier concentration and electrical conductivity), and thermal conductivity of each were measured by the same methods as in Example 1. Table 4 shows the measured values at 1100K and the Figure of merit ($ZT = S^2T/\rho \kappa$).

【0042】

Example 3

In order to produce p- and n-type silicon thermoelectric semiconductors, high-purity silicon (10N) and added elements were compounded as shown in Table 5, after which this product was put in a graphite crucible and melted in a high-frequency melting furnace in a vacuum (10^{-4} Torr), and it was confirmed that the components melted uniformly at approximately 1800K.

【0043】

After this, the upper part of the above-mentioned graphite crucible was lowered to 1700K, silicon seed crystals were brought into contact with the top of the melt, and the melt was slowly pulled up. The inside diameter of

the crucible was 100 mm, the pulling rate was 0.3 to 1 mm/sec, and the pulled crystals were vibrated once every five seconds in order to render them polycrystalline. The average crystal grain size of the obtained material was approximately 1 to 10 μ m.

【0044】

The samples thus obtained were cut to sizes of 5 × 5 × 15 mm, 10 × 10 × 2 mm, and 10 (outside diameter) × 2 mm, and the Seebeck coefficient, Hall coefficient (including carrier concentration and electrical conductivity), and thermal conductivity of each were measured by the same methods as in Example 1. Table 6 shows the measured values at 1100K and the Figure of merit ($ZT = S^2T / \rho \kappa$).

【0045】

【Table 1】

No.	Added element	Added amount (at%)	Added element	Added amount (at%)	Melting temp. (K)	Cooling rate (K/sec)	Crystal grain size (μm)
1	B	0.3			1900	50	100
2	Al	1			1900	50	100
3	Ge	3	B	0.3	1900	50	100
4	Ge	3	B	0.3	1900	100	50
5	Ge	3	Ga	1	1900	50	100
6	P	1			1900	50	100
7	As	1			1900	50	100
8	Ge	3	P	1	1900	50	100
9	Ge	3	P	1	1900	100	50
10	Ge	3	Sb	3	1900	50	100

【0046】

【Table 2】

No.	Seebeck coefficient (mV/K)	Electrical resistivity $\times 10^{-5}$ ($\Omega \cdot m$)	Thermal conductivity (W/m · K)	Figure of merit (ZT)
1	0.267	1.15	37	0.18
2	0.231	1.24	45	0.11
3	0.272	1.18	12	0.57
4	0.286	1.25	9	0.80
5	0.291	1.37	10	0.68
6	-0.301	1.24	42	0.19
7	-0.318	1.31	48	0.18
8	-0.305	1.28	12	0.67
9	-0.314	1.33	9	0.91
10	-0.332	1.42	10	0.85

【0047】

【Table 3】

No.	Added element	Added amount (at%)	Added element	Added amount (at%)	Melting temp. (K)	Cooling rate (K/sec)	Crystal grain size (μm)
11	B	0.3			1900	30	250
12	Al	1			1900	30	250
13	Ge	3	B	0.3	1900	50	100
14	Ge	3	B	0.3	1900	30	250
15	Ge	3	B	0.3	1900	10	500
16	Ge	3	Ga	1	1900	30	250
17	P	1			1900	30	250
18	As	1			1900	30	250
19	Ge	3	P	1	1900	50	100
20	Ge	3	P	1	1900	30	250
21	Ge	3	P	1	1900	10	500
22	Ge	3	Sb	3	1900	30	250

【0048】

【Table 4】

No.	Seebeck coefficient (mV/K)	Electrical resistivity $\times 10^{-5}$ ($\Omega \cdot m$)	Thermal conductivity (W/m · K)	Figure of merit (ZT)
11	0.272	1.08	42	0.18
12	0.234	1.18	48	0.11
13	0.278	1.16	14	0.52
14	0.280	1.12	13	0.59
15	0.282	1.09	12	0.67
16	0.294	1.33	12	0.60
17	-0.309	1.20	48	0.18
18	-0.321	1.29	52	0.17
19	-0.306	1.25	14	0.59
20	-0.309	1.21	13	0.67
21	-0.312	1.19	12	0.75
22	-0.337	1.40	12	0.74

【0049】

【Table 5】

No.	Added element	Added amount (at%)	Added element	Added amount (at%)	Pulling temp. (K)	Pulling rate (mm/sec)	Crystal grain size (mm)
31	B	0.3			1900	0.3	3
32	Al	1			1900	0.3	3
33	Ge	3	B	0.3	1900	1	1
34	Ge	3	B	0.3	1900	0.3	3
35	Ge	3	B	0.3	1900	0.1	9
36	Ge	3	Ga	1	1900	0.3	3
37	P	1			1900	0.3	3
38	As	1			1900	0.3	3
39	Ge	3	P	1	1900	1	1
40	Ge	3	P	1	1900	0.3	3
41	Ge	3	P	1	1900	0.1	9
42	Ge	3	Sb	3	1900	0.3	3

【0050】

【Table 6】

No.	Seebeck coefficient (mV/K)	Electrical resistivity $\times 10^{-5}$ ($\Omega \cdot \text{m}$)	Thermal conductivity (W/m · K)	Figure of merit (ZT)
31	0.275	1.05	45	0.18
32	0.237	1.14	51	0.11
33	0.280	1.19	17	0.43
34	0.283	1.13	15	0.52
35	0.285	1.10	14	0.58
36	0.298	1.30	14	0.54
37	-0.311	1.17	51	0.18
38	-0.324	1.26	54	0.17
39	-0.309	1.22	16	0.54
40	-0.311	1.20	14	0.63
41	-0.315	1.18	13	0.71
42	-0.339	1.38	13	0.70

【0050】

【Effects of the Invention】

Silicon, the main component of the thermoelectric conversion material of the present invention, is an outstanding material in terms of protecting the global environment and conserving the earth's resources, and also affords excellent safety. Furthermore, it is light (has a low specific gravity), which makes it very favorable for thermoelectric conversion elements used in automobiles. Bulk silicon also has good corrosion resistance, which is an advantage in that no surface treatment or the like is needed.

【0052】

Because it makes use of silicon as its main component, the thermoelectric conversion material of the present invention is less expensive than Si-Ge-based materials containing large quantities of costly germanium, and provides a higher Figure of merit than Fe-Si-based materials. Furthermore, the silicon used in the present invention is much lower in purity than that used in semiconductor devices, so the raw material is available at relatively low cost, the result of which is a thermoelectric conversion material with good productivity, stable quality, and low cost.

【0053】

The thermoelectric conversion material of the

present invention takes full advantage of the characteristics of silicon, namely, its low electrical resistance and large Seebeck coefficient despite having a large carrier concentration, and also greatly ameliorates its drawback of high thermal conductivity, and is therefore an effective way to obtain a material with a high Figure of merit. Another advantage is that the properties can be controlled by means of the type and amount of added elements.

【Brief Explanation of Drawings】

【Fig. 1】

Fig. 1 is a photograph taken by EPMA of the crystal structure of the thermoelectric conversion material of the present invention, where A shows the segregation of a germanium added element, and B shows the segregation of a phosphorus added element.

【Fig. 2】

Fig. 2 is a schematic diagram illustrating the crystal structure of the thermoelectric conversion material of the present invention.

【Name of Document】 Summary

【Summary】

【Objects】 It is to improve performance or further enhance the Seebeck coefficient by having a high Seebeck coefficient provided with a novel silicon-based thermoelectric conversion material in which various added elements are contained in silicon at an amount of 20 at% or less, and by decreasing further the thermal conductivity without decreasing an electrical conductivity of the material.

【Means for solving】 By making a structure wherein an added element-rich phase dispersed in the grain boundary of a silicon-rich phase, it is possible to obtain an extremely large Seebeck coefficient and low thermal conductivity, allowing the thermoelectric conversion rate to be raised dramatically, and to obtain a polycrystal silicon-based thermoelectric conversion material composed chiefly of silicon, which is an abundant resource, and which causes extremely little environmental pollution.

【Selected Figure】 Fig. 2

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